**Table I.** Activation Energy for Cyclization of Some cis-Hexatrienes and Their Analogs to Six-Member Rings

System	E_a, kcal/mol
	29.9[a]
	9.4[b]
	20
	~14.2[e,f]

[a] Reference 1a. [b] This work. [c] Reference 3. [d] See Schiess, et al., in ref 4 for similar systems. [e] Estimated from data in ref 8 assuming log A = 12. [f] See also Hobson in ref 11.

trapped by methanol, as hypothesized by Chapman based on product analyses in pyrone systems.[20]

By contrast with the extraordinarily rapid rate of closure of **2**, we note here that the ketene **4** (λ_{max} 397
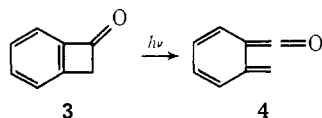
nm, $\nu_{C\equiv O}{}^{Ar}$ = 2120 cm^{-1}),[21] derived from irradiation of benzocyclobutenone, does not show any decay to starting material during the time scale of our flash experiment.[23] Kinetic spectroscopic studies of these and other ketenes are continuing, which we view as a natural complement to our matrix studies of transients in organic photochemistry.

(20) C. L. McIntosh and O. L. Chapman, *J. Amer. Chem. Soc.*, **95**, 247 (1973).

(21) The ultraviolet spectrum of 4 was first obtained by irradiating solutions of 3 (0.01 M) in a 1:1 ether–methylcyclohexane glass at 77°K.[22] A preliminary investigation of the spectrum of the primary product of irradiation (laser excitation wavelength at 265 or 353 nm) of 3 in cyclohexane yielded a similar spectrum which we attribute to 4.

(22) J. Frank, A. Krantz, and S. L. Murov, unpublished results.

(23) The lifetime of 4 must therefore be greater than 500 μsec at 26°.

(24) On leave of absence from Department of Chemistry, State University of New York at Stony Brook, Stony Brook, N. Y. 11790.

A. Krantz[24]

*Laboratorie de Photophysique Moléculaire, Université de Paris-Sud 91 Orsay, France*

Effect of Ligand Solvation on the Stability of Metal Complexes in Solution. An Explanation of the Macrocyclic Effect

Sir:

Some macrocyclic ligands in aqueous solution form more stable complexes with metal ions than open-chain ligands with the same donor groups. This has been

termed the *macrocyclic effect*[1] or *multiple juxtapositional fixedness*[2] in order to distinguish it from the well-known chelate effect because there is an additional enhancement in stability beyond that expected from the gain in translational entropy when chelates replace coordinated solvent from metal ions. Thus, there is more than a 10^6-fold increase in the stability constant of Ni^{II}(cyclam), I, compared to Ni^{II} (2,3,2-tet), II.

I
Ni(cyclam)$^{2+}$

II
Ni(2,3,2-tet)$^{2+}$
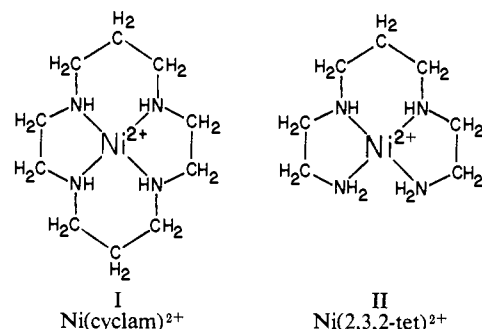
It is not reasonable to assign this large increase in stability to stronger Ni–N bonds in the cyclam complex. Although cyclam has more secondary amine donors than 2,3,2-tet, secondary amines, in general, form less stable Ni^{2+} complexes than primary amines. Furthermore, the difference in the $\Delta H°$ values for the formation of Ni(2,3,2-tet)$^{2+}$ and Ni(en)$_2{}^{2+}$ is small.[3] Obviously the macrocyclic ring cannot force a better coordination geometry than that which the open-chain ligand is free to adopt. Neither ligand can be regarded as very restrictive as there is no evidence of unfavorable ring conformations or of an unusual nickel-nitrogen geometry in the crystal structure of Ni(cyclam)Cl$_2$.[4]

Some correlations have been made between bond strength and electronic absorption bands[5] but both I and II have a λ_{max} at 450 nm. Neither Ni(cyclam)$^{2+}$ nor Ni(2,3,2-tet)$^{2+}$ has appreciable steric hindrance that would prevent the coordination of axial water molecules. The Ni(cyclam)$^{2+}$ complex exists primarily as the yellow square-planar complex in aqueous solution while Ni-(2,3,2-tet)$^{2+}$ exists as a mixture of the blue octahedral complex and the yellow square-planar complex.[6,7] If a correction is made so that the stability constants are compared for only the square-planar complexes in each case then Ni(cyclam)$^{2+}$ has a larger stability constant than [Ni(2,3,2-tet) (square planar)]$^{2+}$ by a factor of 10$^{6.8}$.

On the other hand it might seem quite reasonable to assign the macrocyclic effect to differences in configurational entropy because a greater loss in entropy would be expected in the reaction of the open-chain ligand to form its complex than in the reaction of the macrocyclic ligand to form its complex. If these were gas phase reactions there certainly would be less of a loss in entropy in the latter case.

(1) D. K. Cabbiness and D. W. Margerum, *J. Amer. Chem. Soc.*, **91**, 6540 (1969).

(2) D. H. Busch, K. Farmery, V. Goedken, V. Katovic, A. C. Melnyk, C. R. Sperati, and N. Tokel, *Advan. Chem. Ser.*, No. **100**, 44 (1971).

(3) T. Davies, S. S. Singer, and L. A. K. Staveley, *J. Chem. Soc.*, 2304 (1954); I. Poulsen and J. Bjerrum, *Acta Chem. Scand.*, **9**, 1407 (1955); F. Holmes and D. R. Williams, *J. Chem. Soc. A*, 1702 (1967); M. Ciampolina, P. Paoletti, and L. Sacconi, *J. Chem. Soc.* 4553 (1960).

(4) B. Bosnich, R. Mason, P. J. Pauling, G. B. Robertson, and M. L. Tobe, *Chem. Commun.*, 97 (1965).

(5) P. Paoletti, L. Fabbrizzi, and R. Barbucci, *Inorg. Chem.*, **12**, 1961 (1973).

(6) R. G. Wilkins, R. Yelin, D. W. Margerum, and D. C. Weatherburn, *J. Amer. Chem. Soc.*, **91**, 4326 (1969).

(7) D. C. Weatherburn and D. W. Margerum, unpublished work.

The results of our equilibrium and calorimetric studies show (Table I) that the greater stability of the

Table I. Stability Constants, Enthalpy, and Entropy of Formation of the Nickel Complexes of 2,3,2-tet and cyclam at 25.0° and $\mu = 0.1$

Complex	log K_{NiL}	$\Delta H°$, kcal/mol	$\Delta S°$, cal/ (°K mol)
Ni(2,3,2-tet)$^{2+}$ [a,f,g]	15.8	-19.4 ± 0.1 [b,h]	7.4
[Ni(2,3,2-tet) (sq planar)]$^{2+}$ [c]	15.4	-16.8 ± 0.5	14
Ni(cyclam)$^{2+}$	22.2 ± 0.2 [d,i]	-31.0 ± 0.6 [e,h,i]	-2

[a] Log K_{NiL} is 16.4 in 0.5 M KCl (see footnote f) and is corrected to $\mu = 0.1$ (see footnotes f and g). [b] Determined by calorimetry using the reaction with CN$^-$ and $\Delta H°$ for Ni(CN)$_4^{2-}$. [c] Log K, $\Delta H°$, and $\Delta S°$ are corrected for the blue $\rightleftarrows$ yellow equilibrium (ref 7). [d] Determined spectrophotometrically using CN$^-$ and correcting for the Ni(cyclam)CN$^+$ and Ni(cyclam)OH$^+$ complexes.[9] [e] Determined from the temperature dependence (10.0–40.0°) of the equilibrium constants.[9] [f] D. C. Weatherburn, E. J. Billo, J. P. Jones, and D. W. Margerum, *Inorg. Chem.*, **9**, 1557 (1970). [g] L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Chem. Soc.*, 5115 (1961). [h] J. J. Christensen, R. M. Izatt, J. D. Hale, R. T. Pack, and G. D. Watt, *Inorg. Chem.*, **2**, 337 (1963). The $\Delta H°$ value for Ni(CN)$_4^{2-}$ is interpolated to $\mu = 0.1$ from the tabulated values at ionic strengths of 0.082 and 0.134. [i] G. B. Kolski and D. W. Margerum, *Inorg. Chem.*, **7**, 2239 (1968).

macrocyclic complex actually is due to a more favorable change in $\Delta H°$ (a difference of -14 kcal/mol) which overcomes a less favorable change in $\Delta S°$ (a difference of -16 cal/(°K mol)) for the reaction. Up to this point the effect of ligand solvation has been neglected. In fact, ligand solvation has generally been ignored in the consideration of the thermodynamics of metal complexation reactions. However, for the reaction in eq 1 where the primary solvation (y) of the ligand L is

$$Ni(H_2O)_x{}^{2+} + L(H_2O)_y \longrightarrow NiL(H_2O)_z{}^{2+} + (x + y - z)H_2O \quad (1)$$

variable, the $\Delta H°$ value for the reaction will increase (be less negative) as the enthalpy of solvation of L increases and the $\Delta S°$ value will increase as y increases due to the additional H_2O molecules which are released in the reaction.

We propose that $\Delta H°$ is much more negative for the complexation of cyclam because this ligand is less solvated by water than is 2,3,2-tet. Cyclam is not able to accommodate as many hydrogen-bonded water molecules with its nitrogen donor atoms because of steric hindrance. However, the primary solvation should be the same for both Ni(cyclam)$^{2+}$ and Ni(2,3,2-tet)$^{2+}$. The result is that for cyclam less enthalpic energy need be expended in breaking hydrogen bonds with the solvent ($\Delta H° \simeq 7$ kcal/mol)[8] and a more favorable $\Delta H°$ change is found for reaction 1. It follows that $\Delta S°$ must be less positive for the cyclam reaction than for the 2,3,2-tet reaction because fewer water molecules are released from the ligand.

A difference of two in the number of ligand-solvating water molecules (y) accounts for the difference in $\Delta H°$ values of the cyclam and 2,3,2-tet reactions. The

(8) H. Fritzshe, *Ber. Bunsenges. Phys. Chem.*, **68**, 459 (1964); E. M. Arnett, L. Joris, E. Mitchell, T. S. S. R. Murty, T. M. Gorrie, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 2365 (1970); R. A. Hudson, R. M. Scott, and S. N. Vinogradov, *Spectrochim. Acta, Part A*, **26**, 337 (1970); A. D. H. Clague, G. Govil, and H. S. Bernstein, *Can. J. Chem.*, **47**, 625 (1969); P. A. Kollman and L. C. Allen, *J. Amer. Chem. Soc.*, **93**, 4991 (1971). Average values of $\Delta H°$ and $\Delta S°$ were used.

difference in the $\Delta S°$ values for the two reactions (16 cal/(°K mol)) is less than would be predicted for the release of two water molecules. This can be attributed to the configurational entropy difference of the ligands and the $\Delta S°$ value of $+14$ cal/(°K mol) for the 2,3,2-tet reaction would be even larger compared to cyclam were it not for the greater loss of configurational entropy of the open-chain ligand.

The postulated ligand solvation effect permits several predictions. The macrocyclic effect should be independent of the metal as long as there is not an unfavorable geometry in the coordination of the metal ion within the macrocycle. Thus, very similar enhancements of the stability constants are found for Cu^{2+} and Ni^{2+} with hexamethyl derivatives of cyclam.[9] If the solvent is changed to one with weaker primary solvation of the ligand then the importance of the solvation effect will diminish and the relative contribution due to the configurational entropy will increase. Preliminary results support this prediction.[10]

The predicted ligand solvation effects are not restricted to macrocyclic ligands but will hold for any ligands where the donor groups are forced to be close to one another or in some way are shielded from solvation. In this respect the terminology of multiple juxtapositional fixedness, although awkward, is appropriate. Thus, the effect of ligand solvation on metal stability constants should be particularly important in biological systems. Obviously, the magnitude of metal ion binding constants to proteins and other biological species may be very much influenced by solvation and could differ from that of smaller, more flexible molecules by very large factors. Finally, there are many small variations in the stability constants of coordination complexes which have been explained by a variety of other postulated effects. These now need to be reexamined in view of the possible magnitude of ligand solvation effects.

(9) F. P. Hinz and D. W. Margerum, *Inorg. Chem.*, in press.
(10) G. F. Smith and D. W. Margerum, to be submitted for publication.

Frederick P. Hinz, Dale W. Margerum*
Department of Chemistry, Purdue University
West Lafayette, Indiana 47907
Received April 9, 1974

Rhodium(I) Dithiolene Complexes. Synthesis, Structure, and Dynamic Behavior

Sir:

Studies of Rh(I) complexes have been stimulated by their role in homogeneous catalytic reactions and the related oxidative addition chemistry. To date, the overwhelming majority of these systems are neutral or cationic[1] with few exceptions such as Rh(CO)$_2$Cl$_2^-$ [2a]

(1) See, for example, (a) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Interscience, New York, N. Y., 1973, p 1018; (b) C. K. Brown and G. Wilkinson, *J. Chem. Soc. A*, 2753 (1970), and references therein; (c) M. Green, T. A. Kuc, and S. H. Taylor, *ibid.*, 2334 (1971); (d) R. R. Schrock and J. A. Osborn, *J. Amer. Chem. Soc.*, **93**, 3089 (1971); (e) L. M. Haines, *Inorg. Nucl. Chem. Lett.*, **5**, 399 (1969); *Inorg. Chem.*, **9**, 1517 (1970).
(2) (a) L. M. Vallarino, *Inorg. Chem.*, **4**, 161 (1965); (b) N. G. Connelly and J. A. McCleverty, *J. Chem. Soc. A*, 1621 (1970).